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GRAVIMETRIC ANALYSIS, IONIC COMPOSITION, AND ASSOCIATED WATER MASS OF THE MARINE AEROSOL

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Abstract—Measurements of the total aerosol mass and ionic composition were obtained for submicrometer ($D_p \leq 1.0 \mu\text{m}$) aerosol particles from the remote Pacific boundary layer by gravimetric and ion chromatography analysis. Discrepancies were found to exist between the absolute mass determined by the separate techniques suggesting aerosol components in addition to sea salt and sulfate particles exist at significant mass concentrations. The gravimetric mass was equal to or significantly larger than the sum of the ionic masses, suggesting additional aerosol components contribute between 0 and 75% of the submicrometer aerosol mass. Measurements of the elemental composition of individual particles by electron microscopy confirmed the presence of mineral and carbonaceous particles which contributed 0–86% of the total number concentration for the particle-size range of interest. The relative number of submicrometer sulfate particles with respect to the total was low during periods with the largest discrepancy between the gravimetric and ionic mass. The amount of water associated with the submicrometer aerosol at 47% relative humidity made up 29% of the total aerosol mass collected on the filters (and 9% of the total mass at 35%). Laboratory studies determined the relative amount of water associated with sea salt, sulfate, and sodium chloride particles on a filter substrate, with sea-salt particles containing 27% water and ammonium sulfate particles containing only 4% water at 40% r.h.

Key word index: Aerosol mass, ionic composition, aerosol water, submicrometer particles, Pacific atmosphere, sea salt, sulfate particles.

INTRODUCTION

It is expected that the mass of the submicrometer aerosol ($D_p \leq 1.0 \mu\text{m}$) in the remote marine boundary layer is dominated by the mass of sulfate particles in the form of sulfuric acid, ammonium bisulfate, and/or ammonium sulfate, while the mass of the supermicrometer aerosol ($D_p > 1.0 \mu\text{m}$) is dominated by the mass of sea-salt particles (Cunningham and Zoller, 1981). Even in the remote environment where the contribution from anthropogenic material is small, aerosol mass concentrations can vary significantly in relation to local production mechanisms. The sea-salt component varies strongly with wind speed, fetch and vertical mixing over the ocean and also with height. The tail of the size distribution for mechanically generated sea-salt particles can be extended into the sub-

micrometer size range (O'Dowd and Smith, 1993) and influence the relative number and mass concentration of the accumulation mode aerosol. The relative number concentration of sea salt particles in the size range 0.05–1.0 μm is 4–13% of the total (McInnes *et al.*, submitted). The relative contribution of sea salt to the submicrometer aerosol mass and light scattering may be higher when its median diameter exceeds that of the sulfate aerosol. If sulfate and sea-salt particles are the major contributors to the submicrometer aerosol mass, then the gravimetric mass and the ionic mass of the major water soluble cations and anions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) should agree within the instrumental errors of the analytical techniques for dry aerosol samples. Downwind of continental and especially industrialized areas, other compounds may have substantial and

variable concentrations and their contribution to the total aerosol mass should be significant.

Relatively, few measurements of submicrometer aerosol mass have been reported for the remote marine atmosphere, presumably for the following reasons. Low aerosol mass concentrations exist for the submicrometer marine aerosol, estimated in this work at values between 0.3 and $1.9 \mu\text{g m}^{-3}$, which are an order of magnitude (or more) below the mass of the coarse marine aerosol (Winkler, 1988), and as much as two orders of magnitude below the mass of the submicrometer urban aerosol. The detection limits for gravimetric analysis are not as sensitive as methods used for chemical analysis. Courtney *et al.* (1982) estimated the precision of gravimetric determinations at $22 \mu\text{g}$ per filter (Teflon filter, 25 mm diameter), while the standard deviation of repetitive weighings for Nuclepore filters (47 mm diameter) has been reported at $7 \mu\text{g}$ per filter (Feeney *et al.*, 1984). Therefore, the lowest detectable mass using such techniques is $20 \mu\text{g}$ of material per filter. The detection limit for the SO_4^{2-} ion by ion chromatography can be as low as 0.3 ng per filter, however. When the limitations of the gravimetric determination are coupled with the short sampling times desired for aerosol collection during stable meteorological conditions (4–24 h), the final mass reported may be uncertain by 10–50% of its value.

Measurements of size-dependent aerosol mass concentration have been reported for the boundary layer Atlantic atmosphere at values of $1 \mu\text{g m}^{-3}$ (diameter range 0.2–0.6 μm) and $2 \mu\text{g m}^{-3}$ (diameter range 0.6–2.0 μm) (Winkler, 1988). Aerosol mass measurements from Mauna Loa Observatory were low at 0.26 (upslope conditions) and $0.16 \mu\text{g m}^{-3}$ (downslope conditions) (Pueschel *et al.*, 1973). Often the sum of the chemically analyzed masses is substituted for direct measurement of total aerosol mass, assuming all abundant chemical species have been quantified. However, the total aerosol mass determined by gravimetric analysis and the sum of the chemically analyzed masses do not generally agree within the experimental error indicating, not unexpectedly, that some additional aerosol components are present and not accounted for by the chemical analysis.

Other aerosol components which may contribute to the total mass include inorganic carbon as soot particles, mineral particles, and condensed organic material. The mass of crustal material in the submicrometer size range is normally low, estimated at less than 50 ng m^{-3} for samples collected from the boundary layer of the North Pacific Ocean (Duce *et al.*, 1983). Concentrations of soot and organic material is highly variable, dependent on the air mass history. Measurements of soot concentrations as low as a few ng m^{-3} and as high as 200 ng m^{-3} were obtained along a latitudinal transect (160° W) in the Pacific Ocean (Clarke, 1988). Organic material may exist either as homogeneous particles, organic material incorporated within the particles, or as an insoluble

surface layer. The mass of organic material was estimated at 10 to 20% of the total mass, for remote continental aerosols (Cahill *et al.*, 1989). The relative mass of organic material for marine influenced samples collected in Puerto Rico was estimated at concentrations equal to non-sea-salt sulfate (Novakov and Penner, 1993).

The contribution of condensed or unbound water to the aerosol mass must be considered, given the hygroscopic nature of marine aerosol particles. Aerosol water associated with hygroscopic particles will contribute to the total mass resulting in discrepancies between the gravimetric mass and that determined by ion chromatography. Sodium chloride and ammonium sulfate particles are known to deliquesce at 75 and 80% relative humidity (r.h.), respectively (Tang and Munkelwitz, 1991; Tang *et al.*, 1978), while mixed salt aerosols, such as NaCl–KCl (possibly more representative of the chemistry of sea salt than pure NaCl), deliquesce at a lower relative humidity than the pure salts (Tang *et al.*, 1978).

Decreasing relative humidity, be it in the atmosphere or laboratory, to values below the deliquescence point of the solution droplet, will cause the droplet to become supersaturated. The relative humidity at which the solution droplet crystallizes will be lower and much less definite than its corresponding deliquescence point due to the formation of a supersaturated metastable droplet. Sodium chloride and ammonium sulfate particles crystallize at values of 45 and 39% r.h., respectively (Hameri *et al.*, 1992; Tang and Munkelwitz, 1991). Although the point at which crystallization occurs is important for laboratory studies, ambient sea salt and sulfate particles will probably never be exposed to low relative humidity conditions while in the marine boundary layer. The upper and lower bounds of aerosol water associated with a mixed aerosol of $\text{H}_2\text{SO}_4 \cdot \text{NaCl} \cdot \text{NH}_3 \cdot \text{HNO}_3$ (relative weight composition of 8:5:4:10) was modeled by Pilinis *et al.* (1989), demonstrating that over the range of 20 to 50% r.h., 0–30% of the total aerosol mass was water. Although the aerosol composition used in this model is representative of an urban locality, the results emphasize the importance of aerosol water as a significant contributor to the total mass for deliquescent compounds of atmospheric interest.

EXPERIMENTAL OBJECTIVES

The following measurements provide a substantial data set of aerosol mass concentrations for the remote Pacific boundary layer and supplement the current inventory with latitudinal and temporal resolution. Measurements from Cheeka Peak, WA (48°18' N, 124°37' W) represent samples collected at the marine/continental interface, where the aerosol mass concentrations and chemistry can be influenced by marine, natural land, and anthropogenic sources. Samples

collected from the Pacific atmosphere along a longitudinal transit from 67° N 140° W to 67° S 140° W often represent a purely marine source. The data also test the internal consistency of mass balance between two independent methods of mass determination, gravimetric analysis of the total mass and chromatography analysis of the ionic mass of the aerosol. The precision of the gravimetric determination was enhanced by temperature and humidity control of the weighing environment in which the filters equilibrated. Mass changes proportional to the amount of water associated with aerosol samples could be observed by changing the relative humidity of the weighing and storage environment. Laboratory sea salt and ammonium sulfate particles served as a surrogate for ambient aerosol samples in which the gravimetric and ionic mass must agree within the experimental errors of the two techniques.

SAMPLE COLLECTION

Cheeka Peak

The collection strategy for aerosol sampling is detailed in the project summary in Table 1. Ambient filter samples for gravimetric and IC analysis were collected during the Pacific Sulfur Stratus Experiment (PSI-3) in April of 1991 at the University of Washington research station at Cheeka Peak. The station is located on the Olympic Peninsula 2 km inland of the Washington coast (48°18' N, 124°37' W) at an altitude of 480 m asl (Fig. 1). Samples were collected at the top of a 7 m tower during conditions of on-shore flow when the aerosol number concentration ($D_p > 14$ nm) was less than 1000 particles cm^{-3} and the wind speeds exceeded 2 m s^{-1} . Aerosol sampling was suspended during rain episodes and periods when the tower was in cloud or fog. Samples were collected at ambient conditions on Millipore Fluoropore filters with a cyclone upstream to remove particles greater than 1.0 μm D_p (Quinn and Bates, 1989). The flow rate through the filter pack was nominally 50 slpm. Sampling was terminated when meteorological conditions changed or when the total volume of air collected exceeded 40 m^3 .

Daily submicrometer and weekly supermicrometer aerosol filter samples for gravimetric and IC analysis were also collected at Cheeka Peak as part of the Cloud and Aerosol Chemistry Experiment (CACHE-1) on May 1993. An automated filter carousel system was used to collect samples from an inlet at the bottom of a 7 m heated stack (where $T_{\text{inlet}} = T_{\text{ambient}} + 10^\circ\text{C}$). A cascade impactor was located upstream of the filter carousel to remove particles larger than 1.0 μm D_p . The flow rate was maintained at 30 slpm with a mass flow controller. The same sampling criteria were met during aerosol sampling, based on on-shore winds and the total particle concentration. The supermicrometer ($1.0 < D_p < 10.0 \mu\text{m}$) aerosol mass and chemical composition was determined from weekly impactor samples collected directly upstream of the filter carousel. Daily aerosol filter samples have been collected continuously at Cheeka Peak since January 1994 using the same automated filter carousel system.

Mid-Pacific Marine Boundary Layer

Filter samples were collected on a NOAA research cruise as part of the Marine Aerosol and Gas Exchange Experiment (MAGE) in February and March of 1992. The cruise track is shown in Fig. 1. Samples for total aerosol mass and ionic composition were collected continuously on the return trip between the latitudes of 11° S and 19° N. Ambient samples were collected from the top of a mast 18 m asl, located at the bow of the ship. Filter packs were equipped with a Millipore Fluoropore filter and a cyclone upstream to remove particles larger than 1.0 μm D_p . Ambient samples were collected at a flow rate of 50 slpm for periods of 24–48 h. Average relative humidities measured during aerosol collection were 60–85%. Samples were collected with the ship directed into the wind when wind speeds were greater than 2 m s^{-1} and total particle number concentrations ($D_p > 14$ nm) were below 1000 particles cm^{-3} .

Filter samples were also collected as part of the NOAA Radiatively Important Trace Species (RITS) cruises in 1993 and 1994. RITS 93 took place in

Table 1. Project summary

| Project | Location | Dates | Collection device | Inlet conditions | Humidity |
|------------|--------------------------------------|--------------------------|--------------------------------|------------------|-----------------------|
| PSI-3 | Cheeka Peak 48°N, 124° W | April 1991 | Filter packs with cyclone | Ambient | 40% r.h. |
| CACHE-1 | Cheeka Peak 48°N, 124° W | May 1993 | Filter carousel with impactors | Heated stack | 40% r.h. |
| Continuous | Cheeka Peak 48°N, 124° W | January to May 1994 | Filter carousel with impactor | Heated stack | 35% r.h. and 10% r.h. |
| MAGE | Pacific Ocean 140° W, 11° S to 19° N | February to March 1992 | Filter packs with cyclones | Ambient | 40% r.h. |
| RITS 93 | Pacific Ocean 140° W, 57° S to 57° N | March to May 1993 | Filter packs with cyclones | Ambient | 48% r.h. and 19% r.h. |
| RITS 94 | Pacific Ocean 140° W, 57° N to 57° S | November to January 1994 | Filter packs with cyclones | Ambient | 48% r.h. and 19% r.h. |
| Lab Study | | | Filter packs | Ambient | 9 to 48% r.h. |

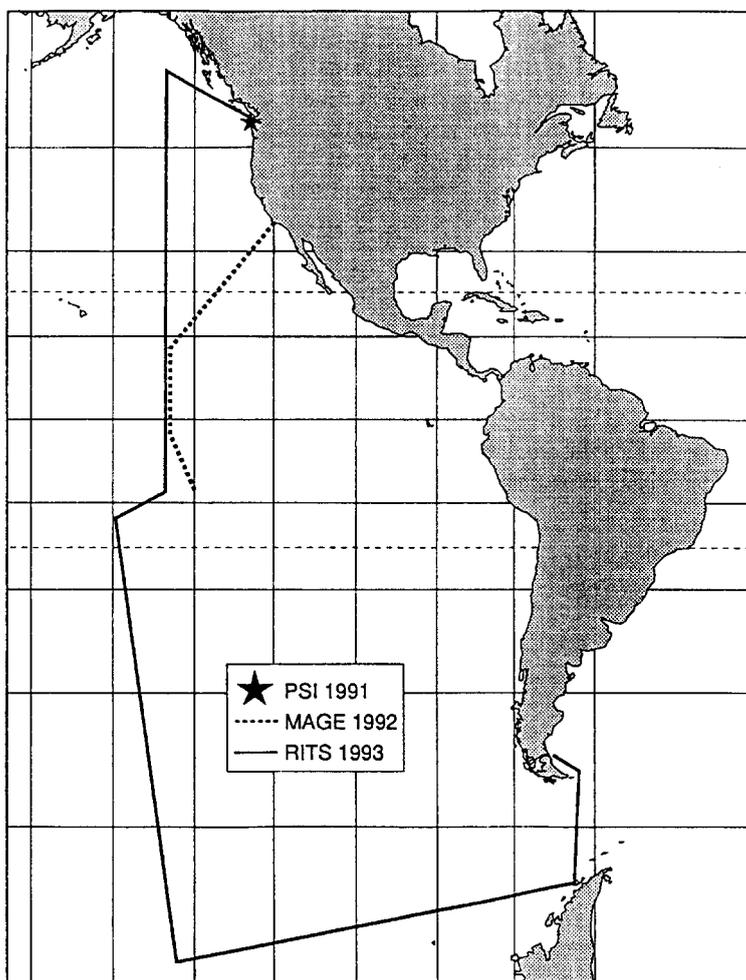


Fig. 1. The University of Washington Cheeka Peak Research Station was the location of the PSI-3 and CACHE-1 experiments. The relative location of the research vessels during the MAGE and RITS experiments in 1993 and 1994 is shown. During the RITS 1994 experiment the cruise track was repeated in the opposite direction, from North to South.

March, April, and May of 1993 and RITS 94 occurred in November, December of 1993 and January of 1994. During both cruises the ship traveled between Punta Arenas, Chile and Seattle, Washington, U.S.A. covering the latitudinal range between 57°S and 57°N as shown in Fig. 1. Ambient aerosol particles were collected from the top of a mast 21 m above the sea surface using the same sampling criteria described above. These projects are summarized in Table 1.

GRAVIMETRIC ANALYSIS

The initial and final weights of the filters (47 mm, $1.0\ \mu\text{m}$ pore size) and Tedlar impactor films (90 mm) were obtained on a microbalance (Mettler UMT2 and Cahn model 29, respectively). During the field experiments (PSI-3, MAGE) the filters were stored in pre-cleaned petri dishes in a desiccator containing Drierite prior to gravimetric analysis. Several pre-

cautions were taken to maintain the accuracy and precision of the gravimetric measurements. The balance was checked periodically (every 10th weight) for instrumental drift with calibration weights which provided a standard reference. Separate weighings of the same filters provided an estimate of the standard deviation (1σ) of repetitive weighings, which was $\pm 3\ \mu\text{m}$ per filter. Balance instabilities attributable to static charging were minimized by exposing filters to a ^{210}Po source. The determination was made at 40% r.h.

During later field experiments (CACHE-1, RITS) the balance was housed in a humidity and temperature controlled chamber situated in a class 100 clean room. Gravimetric measurements were made at relative humidities between 9 and 48% (20°C) using a semi-dynamic method for humidity control (Young, 1967). Clean room air which had been scrubbed for ammonia vapor, acidic gases, and organic vapor circulated over a flat container of a saturated salt

solution. The lowest humidity was achieved with N₂ cylinders which were also scrubbed. The filter pre-weights were determined at 33 ± 2% relative humidity using a saturated solution of MgCl₂·6H₂O. Field blanks representing 20% of the total number of filters were sampled for 1–3 min and handled and stored in the same manner as field samples. Significant changes in the pre-weights of unsampled filters stored for an extended period (6–12 months) were examined. The filters, including blanks, were weighed in batches exposed to decreasing relative humidity from the highest value of 48% to the lowest value of 9%. The filters were weighed in this manner to simulate the decreasing relative humidity through a heated inlet which occurred during aerosol collection in the field.

Measurements of the total submicrometer aerosol mass have been made at Cheeka Peak since January 1994 at 33 and 9% r.h. The water mass associated with the aerosol particles at 33% r.h. has been calculated from the mass difference between the higher and lower relative humidity. Samples collected during RITS in 1994 were also weighed at two humidities, 48% and 19% r.h. The mass of water associated with the aerosol particles at 48% r.h. was determined by the difference in mass obtained at the two humidities assuming the aerosol particles were dry at 19% r.h.

ION CHROMATOGRAPHY ANALYSIS

Aerosol filters were extracted with HPLC grade methanol and deionized water in a 1:5 volume proportion, sonicated, and centrifuged before analysis on a Dionex 2021i Ion Chromatograph. The ionic mass of water soluble anions (Cl⁻, NO₃⁻, and SO₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺) was determined using procedures outlined in Quinn *et al.* (1990). The total sea-salt mass (M_{ss}) for each sample was estimated based on the mass of sodium (M_{Na}) measured on the filter and the relative composition of bulk seawater using equation (1). The relative weight ratios of the major anions and cations in seawater used in equation (1) are reported in Table 2. The Na⁺ ion was used as a conservative tracer

$$M_{ss} = M_{Na} + M_{Na} \times \left[\frac{M_{Cl}}{M_{Na}} + \frac{M_{SO_4}}{M_{Na}} + \frac{M_K}{M_{Na}} + \frac{M_{Ca}}{M_{Na}} + \frac{M_{Mg}}{M_{Na}} \right] \quad (1)$$

for sea salt because atmospheric reactions with individual submicrometer sea-salt particles can liberate the Cl⁻ ion leaving the particles depleted in chloride relative to the seawater composition (McInnes *et al.*, 1994). The total sea salt mass calculated in this manner was verified in most cases with the sum of the sea-salt ions measured from the filter samples. The non-sea-salt (nss) SO₄²⁻ mass was estimated from the total sulfate mass measured on each filter minus the contribution from sea-salt sulfate, calculated from the

Table 2. Ionic composition (> 1%) of bulk and artificial seawater (SW)

| | SW (mg ℓ ⁻¹) | SW (Ratio to Na ⁺) (wt/wt) | Artificial SW (wt/wt) |
|-------------------------------|-----------------------------|---|--------------------------|
| Na ⁺ | 1.05 × 10 ⁴ | 1.000 | 1.000 |
| Cl ⁻ | 1.90 × 10 ⁴ | 1.810 | 1.625 |
| Ca ²⁺ | 4.00 × 10 ² | 0.038 | 0.037 |
| Mg ²⁺ | 1.35 × 10 ³ | 0.129 | 0.082 |
| K ⁺ | 3.80 × 10 ² | 0.036 | 0.045 |
| SO ₄ ²⁻ | 2.66 × 10 ³ | 0.253 | 0.356 |

Seawater (SW) values taken from Holland (1978). Artificial seawater ratios were measured by IC.

Na⁺ ion concentration using the relative weight ratio of SO₄²⁻/Na⁺ in seawater. The NH₄⁺/nss SO₄²⁻ ratio determined for each sample was used to estimate the degree of neutralization of the sulfate particles. The mass of the sulfate particles was approximated by the sum of NH₄⁺ and nss SO₄²⁻ mass, although this does not consider the amount of processed sulfate associated with sea-salt particles.

LABORATORY GENERATED AEROSOLS

Generation of sea salt and sulfate aerosols

Sea salt, ammonium sulfate, ammonium bisulfate, and sulfuric acid particles were generated with a constant output atomizer (TSI model 3076) from a 2% (wt/wt) salt solution. The chemical composition of the artificial sea salt used for the study is shown in Table 2. Salt particles were sampled directly from the atomizer, after the aerosol passed through a diffusion drier and charge neutralizer (⁸⁵Kr source), onto filters using filter packs. Filters were stored in a desiccator prior to gravimetric analysis. The gravimetric mass was determined at 40% r.h. (± 2%). The amount of water associated with the particles was calculated from the difference between the gravimetric and ionic mass, since all the major ions present in the salts were detected with IC analysis. The crystallization humidity for sea-salt, a complex mixture of pure salts, should be lower than pure NaCl and therefore the particles may contain appreciable amounts of water at 40% r.h. At this humidity, sulfuric acid will exist as a 48% (wt/wt) solution (Bray, 1970) and ammonium bisulfate as a 74.2% (wt/wt) solution (Tang and Munkelwitz, 1977). Ammonium sulfate solution droplets crystallize at 39% r.h. (Tang and Munkelwitz, 1991), therefore laboratory particles under the experimental conditions described (40% r.h.) should be dry. The relative chemistry of the generated sea-salt particles matched that of its parent solution, demonstrating no chemical fractionation occurred upon production. In a separate experiment, particles collected on filters (except sulfuric acid) were heated overnight in an oven maintained at 110°C to drive off any remaining water before gravimetric analysis.

Determination of mass changes associated with changing relative humidity

Aerosol mass changes associated with changing relative humidity for lab sea salt, sodium nitrate, ammonium sulfate, ammonium bisulfate, and sulfuric acid particles collected on a filter over the range 48% to 9% r.h. The weights were recorded from high to low relative humidity to simulate drying of the aerosol as it passed through a heated inlet. The relative humidity where the particle mass remained constant was determined. The amount of water associated with the laboratory particles at each relative humidity was determined from changes in mass referenced to the constant mass. Due to the collective behavior of particles on a filter, the amount of water associated with aerosols sampled on a filter may be different from the deliquescence behavior of individual salt particles. Therefore comparison of these data with hygroscopic growth curves obtained for individual particles may not be entirely appropriate depending on surface effects and the degree of external mixing of the ambient aerosol. Winkler (1988) has observed a smooth mass gain with increasing relative humidity for aerosols collected on a filter substrate, rather than the abrupt mass change normally associated with the deliquescence or crystallization of individual particles.

LABORATORY RESULTS

Behavior of filter substrates

The standard deviation (σ) of repetitive weighings ($n > 20$) of the same Millipore filter was $\pm 7 \mu\text{g}$ (Cahn

microbalance) and $\pm 3 \mu\text{g}$ (Mettler microbalance) per filter. The standard deviation of replicate weighings of a Tedlar impaction substrate was $\pm 7 \mu\text{g}$ per impactor film (Cahn microbalance). The relative error associated with filter handling and storage was determined with blank filters stored for a period of 6 to 12 months. The mass change associated with storage was distributed around an average value of 0.004 mg with 92% of the data falling within $\pm 1\sigma$ ($12 \mu\text{g}$) of the average value (Fig. 2). This indicates the filter material maintains a constant weight during storage. Field blanks, which were handled in the same manner as field samples, showed a very similar distribution with a mean value of 0.005 mg and similar standard deviation.

Sea-salt particles

Laboratory sea-salt particles collected on filters contained measurable quantities of water under the conditions of our gravimetric analysis. However, laboratory, sea-salt particles which were dried in an oven overnight at 110°C contained virtually no water associated with the particles. The ionic mass obtained from IC analysis was equal to or at most 10% greater than the gravimetric mass for oven-dried samples. The results indicate the crystallization humidity for sea-salt particles is below the crystallization humidity of pure sodium chloride particles and below the relative humidity of our measurements. The amount of water associated with sea-salt particles when the r.h. decreased to 40% was on average $26 \pm 5\%$ of the total mass (Table 3). In a separate experiment the relative humidity was increased from 9 to 38% causing the

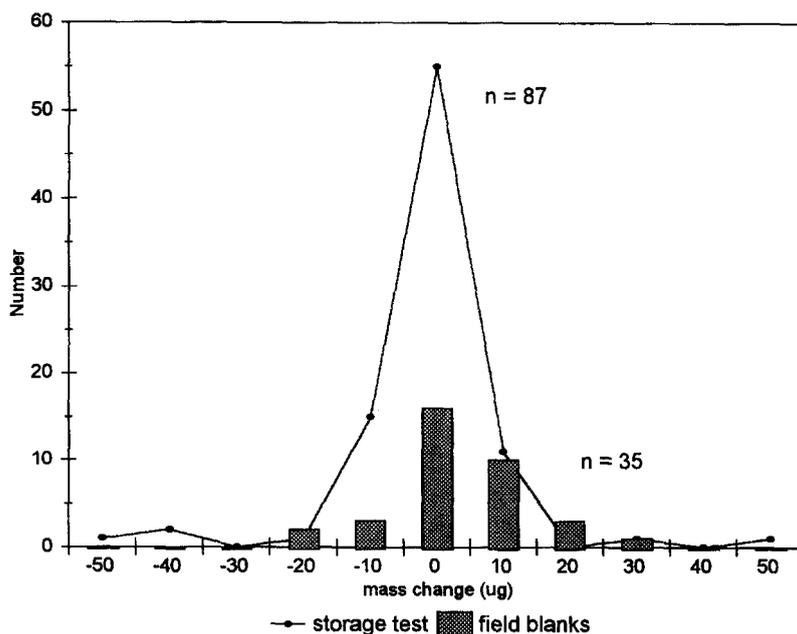


Fig. 2. The mass change associated with extended filter storage for unsampled filters demonstrated 92% of the data fell within $\pm 1\sigma$ of the average value (0.004 mg). Field blanks showed a similar distribution around a mean value of 0.005 mg.

total mass of sea salt, sodium chloride, and sodium nitrate particles to increase as shown in Fig. 3. The mass of sea salt and sodium nitrate particles increased between 9% and 20% r.h., indicating the deliquescence point occurs at a value within this range. The mass of the sodium chloride particles did not change significantly, which is in agreement with the deliquescence point of sodium chloride (Tang *et al.*, 1978). Sea-salt particles collected on a filter were found to contain about 5% water at 22% relative humidity. The crystallization humidity of sea salt and sodium nitrate remains unknown at this time since measurements in the reverse direction from high to low r.h. were not made.

Sulfate particles

The amount of water mass associated with sulfate particles at 40% r.h. is reported in Table 4. The amount of water associated with sulfuric acid particles (collected on a filter) was on average $53 \pm 4.9\%$ at 40% relative humidity, compared with solution data (Bray, 1970) which shows 52% water. As the particle

acidity decreased with the addition of the ammonium ion, the amount of water associated with the particles decreased. Ammonium bisulfate particles collected on a filter contained on average $48 \pm 5.7\%$ of their mass as water at 40% r.h. while solution data (Tang and Munkelwitz, 1977) predicts 25.8%. Ammonium sulfate particles on average contained little to no water ($4 \pm 3.3\%$). In a separate experiment, the change in aerosol mass was determined for the same lab particles with decreasing relative humidity from 48 to 9%. The aerosol growth factors, plotted with respect to the aerosol mass at 9%, are shown in Fig. 4. Acidic sulfate particles contained significant quantities of water at low relative humidity. When the relative humidity decreased to below 40%, the mass of ammonium sulfate remained constant indicating there was no remaining water. When ammonium sulfate particles were examined with increasing relative humidity, no significant change in mass occurred over the same range.

FIELD RESULTS

Aerosol mass concentrations

The submicrometer aerosol mass concentrations and the amount of water associated with the aerosol particles for samples from Cheeka Peak and the remote Pacific atmosphere are presented in Tables 5 and 6, along with the respective sampling locations and day of year. The relative error associated with each gravimetric determination was calculated as 2 times the standard deviation of the field blanks divided by the absolute mass collected on each filter.

Table 3. Water mass associated with lab generated sea-salt particles at 40% r.h.

| Filter | Total mass (mg per filter) | Ionic mass (mg per filter) | Percent water (%) |
|--------|----------------------------|----------------------------|-------------------|
| 1 | 0.6999 | 0.5603 | 19.9 |
| 2 | 0.3799 | 0.2755 | 27.5 |
| 3 | 0.5060 | 0.3436 | 32.1 |
| 4 | 0.3865 | 0.2604 | 32.6 |
| 5 | 0.4315 | 0.3417 | 20.0 |

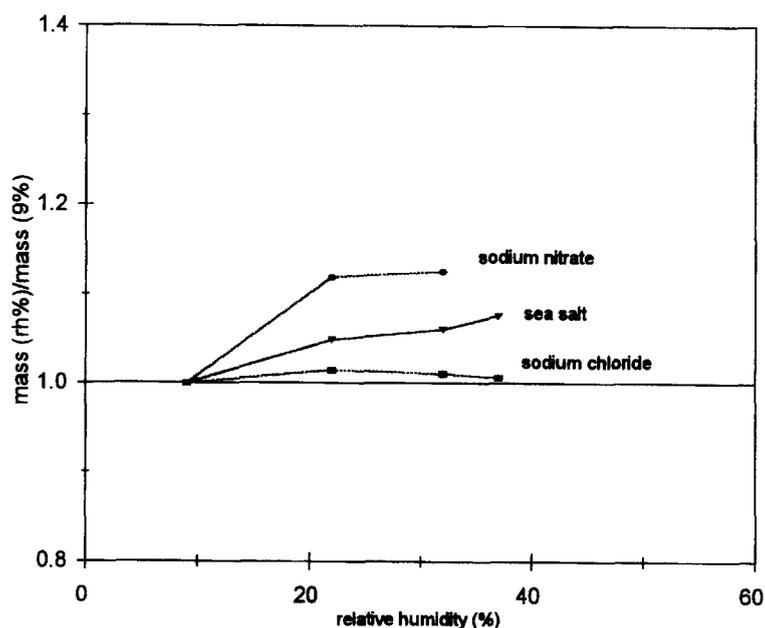


Fig. 3. The mass change associated with increasing relative humidity for sodium nitrate, artificial sea salt, and sodium chloride particles collected on a filter.

The relative error for each sample is strongly dependent on the absolute mass collected on the filter. Only filters which collected an absolute mass in excess of $30 \mu\text{g}$ are included. Because the duration of sample collection varied during the experiments, this does not exclude all samples with low mass concentrations. The submicrometer aerosol mass concentrations were between 0.3 and $4.9 \mu\text{g m}^{-3}$, often with concentrations less than $1 \mu\text{g m}^{-3}$. The samples from PSI-3 (1991), MAGE (1992), and RITS (1993, 1994) experiments were collected at ambient relative humidities. Therefore, the particle-size distribution during collec-

tion represents the hydrated aerosol which upon drying shifts to smaller sizes. Samples obtained at Cheeka Peak after 1991 were collected and weighed at virtually the same relative humidity.

Discrepancies between gravimetric and ion chromatography analysis

Cheeka Peak. The total aerosol mass determined by gravimetric analysis was compared to the total ionic mass determined from IC analysis. The ionic mass for aerosol samples collected at Cheeka Peak during the PSI-3 experiment in the spring of 1991 was less than the gravimetric mass, representing only 31–59% of the total mass as shown in Fig. 5. The hygroscopic properties of the aerosol as a whole were qualitatively consistent, as inferred from gravimetric results under controlled relative humidity conditions. Qualitatively, it varied by a factor of 2 however, which is to be expected as the ratio of ammonium sulfate to sea salt to organic components changes. Air mass trajectories for samples collected between Julian day (JD) 106 and 115 demonstrated the air mass subsided from the free troposphere passing over Canada 2 to 3 days prior to sampling (Quinn *et al.*, 1993). Air mass trajectories for samples collected between JD 115.5 and 119 suggest the air originated from a northwesterly to westerly direction passing over the ocean for several days prior to sampling. The amount of water associated with sea salt and sulfate particles at the

Table 4. Water mass associated with lab generated sulfate particles on a filter at 40% r.h.

| Lab particles | Total mass (mg) | IC mass (mg) | Percent water (%) |
|------------------------------|-----------------|--------------|-------------------|
| H_2SO_4 | 0.154 | 0.080 | 48.4 |
| | 0.191 | 0.102 | 46.4 |
| | 0.256 | 0.125 | 51.3 |
| | 0.105 | 0.044 | 57.9 |
| | 0.100 | 0.042 | 58.5 |
| NH_4HSO_4 | 0.238 | 0.125 | 47.6 |
| | 0.153 | 0.090 | 40.9 |
| | 0.119 | 0.054 | 54.9 |
| $(\text{NH}_4)_2\text{SO}_4$ | 0.071 | 0.074 | 0.0 |
| | 0.048 | 0.046 | 3.2 |
| | 0.078 | 0.072 | 8.1 |

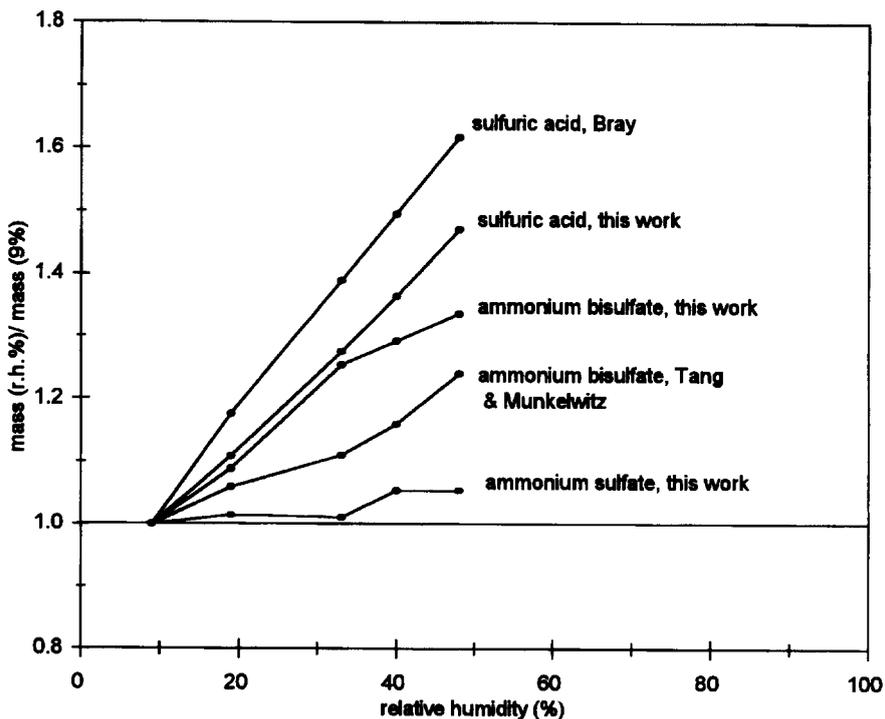


Fig. 4. The change in mass associated with decreasing relative humidity for sulfuric acid, ammonium bisulfate, and ammonium sulfate particles collected on a filter. Reference values for sulfuric acid and ammonium bisulfate solutions are from Bray (1970) and Tang and Munkelwitz (1977).

Table 5. Submicrometer aerosol mass concentrations from samples collected at Cheeka Peak

| Date | Aerosol mass ($\mu\text{g m}^{-3}$) | Water mass ($\mu\text{g m}^{-3}$) | Relative error (%) | Date | Aerosol mass ($\mu\text{g m}^{-3}$) | Water mass ($\mu\text{g m}^{-3}$) | Relative error (%) |
|----------|--|--|-----------------------|----------|--|--|-----------------------|
| 91 04 17 | 0.84 (40% r.h.) | nd | ± 40 | 94 05 08 | 2.38 (9% r.h.) | 0.12 (33%) | ± 13 |
| 91 04 22 | 1.90 (40% r.h.) | nd | ± 18 | 94 05 09 | 1.29 (9% r.h.) | 0.14 (33%) | ± 33 |
| 91 04 24 | 1.00 (40% r.h.) | nd | ± 25 | 94 05 13 | 1.85 (9% r.h.) | 0.14 (33%) | ± 24 |
| 91 04 25 | 1.13 (40% r.h.) | nd | ± 25 | 94 05 15 | 2.40 (9% r.h.) | 0.54 (33%) | ± 40 |
| 91 04 27 | 1.46 (40% r.h.) | nd | ± 12 | 94 05 16 | 2.51 (9% r.h.) | 0.17 (33%) | ± 24 |
| 91 04 29 | 1.09 (40% r.h.) | nd | ± 38 | 94 05 17 | 3.42 (9% r.h.) | 0.36 (33%) | ± 15 |
| 94 02 13 | 1.06 (14% r.h.) | 0.11 (38% r.h.) | ± 43 | 94 05 19 | 4.55 (9% r.h.) | 0.62 (33%) | ± 23 |
| 94 02 14 | 3.36 (14% r.h.) | 0.88 (38% r.h.) | ± 39 | 94 05 21 | 1.47 (9% r.h.) | 0.37 (33%) | ± 35 |
| 94 02 22 | 0.98 (14% r.h.) | 0.16 (38% r.h.) | ± 27 | 94 05 22 | 1.38 (9% r.h.) | 0.26 (33%) | ± 29 |
| 94 03 15 | 2.28 (19% r.h.) | 0.31 (33% r.h.) | ± 27 | 94 05 23 | 1.23 (9% r.h.) | 0.35 (33%) | ± 30 |
| 94 03 18 | 1.01 (17% r.h.) | 0.20 (40% r.h.) | ± 40 | 94 05 24 | 1.84 (9% r.h.) | 0.40 (33%) | ± 31 |
| 94 04 14 | 2.61 (9% r.h.) | 0.30 (33% r.h.) | ± 21 | 94 05 25 | 1.45 (9% r.h.) | 0.37 (33%) | ± 39 |
| 94 04 17 | 4.90 (9% r.h.) | 0.30 (33% r.h.) | ± 20 | 94 05 27 | 1.07 (9% r.h.) | 0.37 (33%) | ± 29 |
| 94 04 24 | 2.21 (9% r.h.) | 0.20 (33% r.h.) | ± 30 | 94 06 01 | 1.44 (9% r.h.) | 0.53 (33%) | ± 43 |
| 94 04 29 | 1.51 (9% r.h.) | 0.23 (33% r.h.) | ± 33 | 94 06 03 | 2.39 (9% r.h.) | 0.57 (33%) | ± 24 |
| 94 04 30 | 1.61 (9% r.h.) | 0.10 (33% r.h.) | ± 19 | 94 06 07 | 0.98 (9% r.h.) | 0.33 (33%) | ± 38 |
| 94 05 07 | 4.84 (9% r.h.) | 0.00 (33% r.h.) | ± 15 | 94 06 08 | 1.52 (9% r.h.) | 0.51 (33%) | ± 27 |

nd = not determined.

Table 6. Submicrometer aerosol mass concentrations from remote Pacific samples

| Position | Aerosol mass ($\mu\text{g m}^{-3}$) | Relative error (%) | Position | Aerosol mass ($\mu\text{g m}^{-3}$) | Water mass ($\mu\text{g m}^{-3}$) | Relative error (%) |
|-------------|--|-----------------------|-------------|--|--|-----------------------|
| 11 S, 140 W | 1.15 (40% r.h.) | ± 7 | 25 N, 140 W | 2.38 (40% r.h.) | nd | ± 4 |
| 4 S, 140 W | 3.26 (40% r.h.) | ± 5 | 36 N, 140 W | 2.67 (40% r.h.) | nd | ± 4 |
| 1 S, 140 W | 3.92 (40% r.h.) | ± 4 | 46 N, 140 W | 1.05 (40% r.h.) | nd | ± 22 |
| 2 N, 140 W | 1.18 (40% r.h.) | ± 25 | 52 N, 136 W | 1.73 (40% r.h.) | nd | ± 8 |
| 8 N, 140 W | 0.33 (40% r.h.) | ± 54 | 50 N, 128 W | 1.15 (40% r.h.) | nd | ± 27 |
| 12 N, 140 W | 0.97 (40% r.h.) | ± 11 | 51 N, 137 W | 0.65 (19% r.h.) | 0.06 | ± 17 |
| 16 N, 140 W | 0.82 (40% r.h.) | ± 14 | 39 N, 140 W | 0.55 (19% r.h.) | 0.10 | ± 37 |
| 19 N, 140 W | 0.96 (40% r.h.) | ± 12 | 25 N, 140 W | 0.79 (19% r.h.) | 0.07 | ± 14 |
| 62 S, 64 W | 1.16 (40% r.h.) | ± 25 | 15 N, 140 W | 0.77 (19% r.h.) | 0.04 | ± 12 |
| 66 S, 69 W | 1.94 (40% r.h.) | ± 6 | 4 N, 140 W | 0.88 (19% r.h.) | 0.15 | ± 12 |
| 66 S, 86 W | 0.98 (40% r.h.) | ± 13 | 3 S, 140 W | 1.32 (19% r.h.) | 0.33 | ± 7 |
| 65 S, 98 W | 0.63 (40% r.h.) | ± 13 | 5 S, 140 W | 1.51 (19% r.h.) | 0.36 | ± 6 |
| 65 S, 113 W | 0.36 (40% r.h.) | ± 50 | 7 S, 140 W | 1.34 (19% r.h.) | 0.31 | ± 7 |
| 51 S, 145 W | 1.04 (40% r.h.) | ± 9 | 13 S, 144 W | 1.16 (19% r.h.) | 0.36 | ± 11 |
| 41 S, 146 W | 0.45 (40% r.h.) | ± 24 | 24 S, 148 W | 0.68 (19% r.h.) | 0.13 | ± 16 |
| 31 S, 147 W | 1.68 (40% r.h.) | ± 8 | 33 S, 146 W | 0.46 (19% r.h.) | nd | ± 34 |
| 23 S, 148 W | 0.94 (40% r.h.) | ± 18 | 41 S, 144 W | 0.31 (19% r.h.) | nd | ± 27 |
| 19 S, 149 W | 0.57 (40% r.h.) | ± 13 | 63 S, 134 W | 0.81 (19% r.h.) | 0.14 | ± 11 |
| 14 S, 145 W | 1.50 (40% r.h.) | ± 6 | 68 S, 121 W | 0.40 (19% r.h.) | 0.06 | ± 25 |
| 6 S, 140 W | 1.09 (40% r.h.) | ± 9 | 68 S, 101 W | 0.69 (19% r.h.) | 0.04 | ± 14 |
| 4 N, 140 W | 1.20 (40% r.h.) | ± 9 | 66 S, 77 W | 1.01 (19% r.h.) | 0.25 | ± 7 |
| 14 N, 140 W | 1.32 (40% r.h.) | ± 7 | 68 S, 64 W | 0.77 (19% r.h.) | 0.25 | ± 17 |

nd = not determined.

time of gravimetric analysis was estimated assuming the particles behaved in a similar fashion as the laboratory particles. The acidity of the sulfate particles was approximated by the $\text{NH}_4^+/\text{nss SO}_4^{2-}$ ratio. However, the total ionic mass including the water correction was not enough to resolve the discrepancy between the two measurements, indicating additional aerosol components were present at 41 to 69% of the total submicrometer aerosol mass.

Samples collected at Cheeka Peak in the spring of 1993 also demonstrated a significant discrepancy between the total aerosol mass and the ionic mass, as

shown in Fig. 6. Again, there is evidence of additional aerosol components which comprised between 48 and 98% of the total submicrometer aerosol mass. Samples collected on JD 133, 135, and 139 were particularly interesting, less than 10% of the aerosol mass was analyzed by ion chromatography, although not representative of the remote Pacific atmosphere. Individual aerosol particles collected during this same time period on JD 133 and 139 were analyzed by analytical electron microscopy. The relative abundance of sea salt, sulfate, and mineral particles represented less than 20% of the total number of

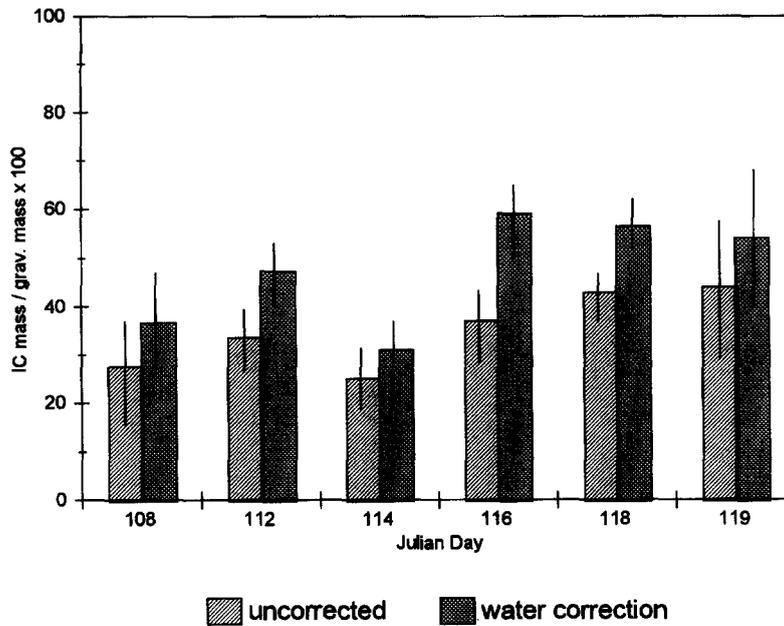


Fig. 5. Samples collected at Cheeka Peak during the PSI-3 experiment in 1991 show a large discrepancy between the ionic mass and total mass determined by gravimetric analysis. The amount of water associated with the aerosol is calculated based on the relative mass of sea salt and sulfate particles. High and low values are shown which reflect the relative error of the determination.

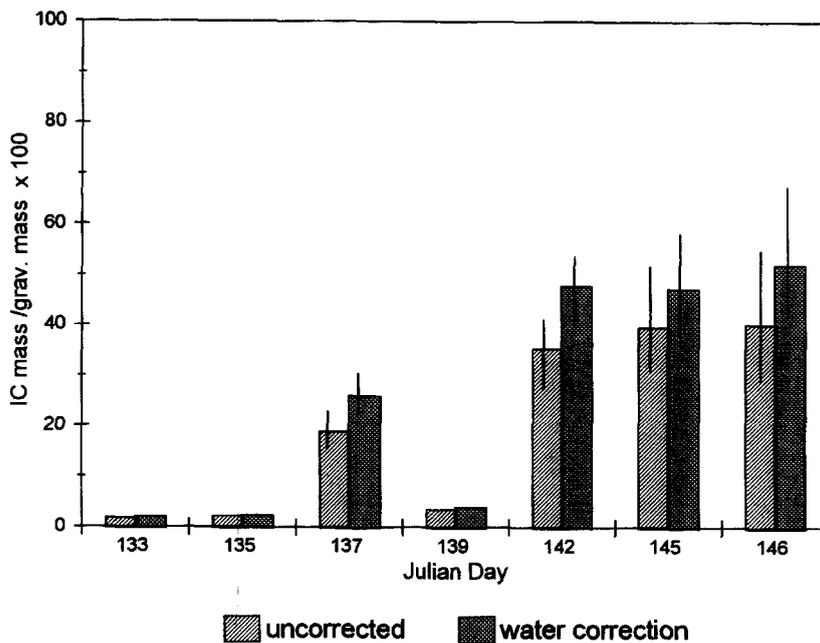


Fig. 6. Samples collected at Cheeka Peak during the CACHE-1 experiment in 1993 show a large discrepancy between the ionic and total mass. Samples collected on Julian day 133, 135, and 139 are not considered representative of purely marine sources.

accumulation mode particles ($50 \text{ nm} \leq D_p \leq 1.0 \text{ }\mu\text{m}$). Elemental spectra of the unidentified particles contained carbon, oxygen and possibly other low Z elements (such as nitrogen) which are not easily identified with the X-ray detector. The particles had

a spherical morphology and did not resemble carbonaceous soot, implying they were probably carbonaceous particles of organic composition.

Mid-Pacific Marine Boundary Layer. Results obtained from the remote Pacific atmosphere during the

MAGE experiment are presented in Fig. 7. The total aerosol mass and ionic mass agree within the errors of the analytical techniques for many of the samples, when the water mass associated with the aerosol is included (water correction). The remaining samples suggest the presence of additional aerosol components contributing between 7 and 59% of the total aerosol mass. The largest discrepancy was associated with samples collected on JD 77 at 2° N, 140° W. During this sampling period the highest concentrations of light absorbing material were recorded for the cruise, indicating the aerosol was not purely from a marine source. The trajectories calculated 5 days back in time suggest the aerosol may have originated over the coast of California (Quinn *et al.*, in press). Due to the low absolute mass concentrations determined for JD 78 (8° N, 140° W) the uncertainty associated with the gravimetric analysis is relatively large.

The agreement between the gravimetric mass and ionic mass for samples collected during RITS are shown in Figs 8 and 9. The gravimetric analysis for the 1994 RITS sample set was performed at both 20 and 40% relative humidity. At 20% r.h. the samples should be dry and the mass discrepancies that exist between the gravimetric and ion chromatographic determination (above the relative error of the measurement) should reflect the amount of additional material associated with the aerosol. For many of the samples, greater than 80% of the total mass was due to sea salt and sulfate components. The gravimetric determination for the 1993 RITS sample set was made at 40% r.h. only. In order to approximate the contribution from water associated with the aerosol par-

ticles, we used the average mass change observed for the RITS 1994 samples over the same cruise track to estimate the dry filter weight at 20% r.h. This is plotted in Fig. 8 as the IC mass to total mass at 20% relative humidity. Again, the total ionic mass was in agreement (80% or greater) with the total mass determined by gravimetric techniques suggesting sea salt and sulfate particles were mostly responsible for the submicrometer mass.

Tests were performed using duplicate samples to determine the error associated with sampling and handling of the filters. The agreement between duplicate samples analyzed by ion chromatography is shown in Fig. 10 demonstrating on average the filters agreed within 10%. The effect of filter storage before gravimetric analysis was examined by comparing the ionic mass determined for filter samples analyzed immediately on-board ship and duplicate ones stored until the gravimetric and IC analysis could be performed back at the laboratory. The results were highly correlated (Fig. 11) with a linear best fit line of the form $y = 0.92x + 0.08$ ($R^2 = 0.917$).

Mass changes associated with changing relative humidity conditions

Cheeka Peak. The total submicrometer aerosol mass for daily filter samples collected at Cheeka Peak between January and June of 1994 was determined at both 35 (± 3)% and 10 (± 4)% r.h. At the lowest relative humidity the aerosol should be dry assuming the major form of sulfate is ammonium bisulfate or ammonium sulfate, which previous research indicates is generally the case (Covert, 1988). At 35% r.h. the

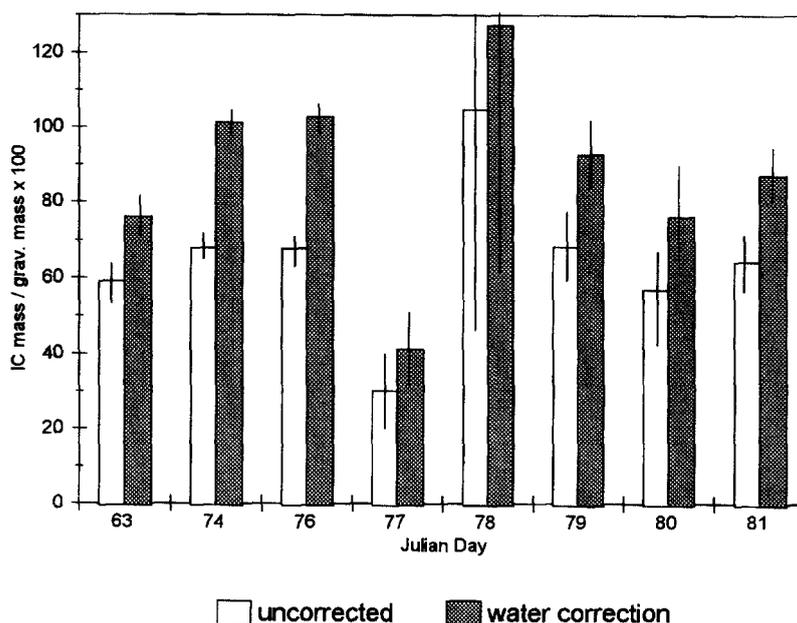


Fig. 7. Samples collected during the MAGE experiment in 1992 have a large fraction of the total mass explained by the mass of sea salt and sulfate material. The sample collected on Julian day 78 has a large error associated with the gravimetric determination due to the low absolute mass collected on the filter.

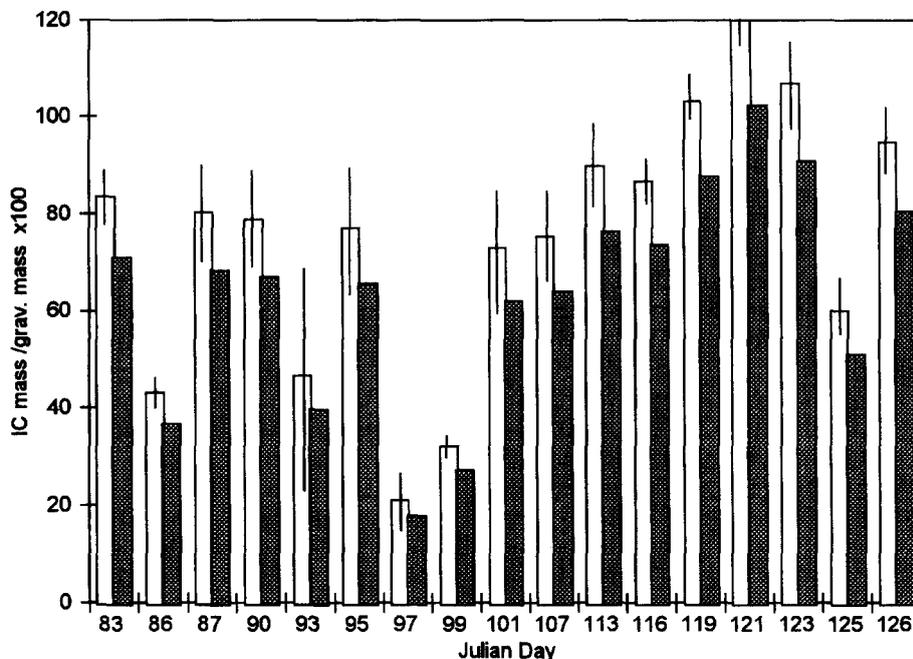


Fig. 8. Comparison of the ionic mass and total mass for samples collected during the RITS experiment in 1993 at 19 and 40% relative humidity. The amount of water associated with the aerosol at 40% was estimated based on results obtained during RITS 1994.

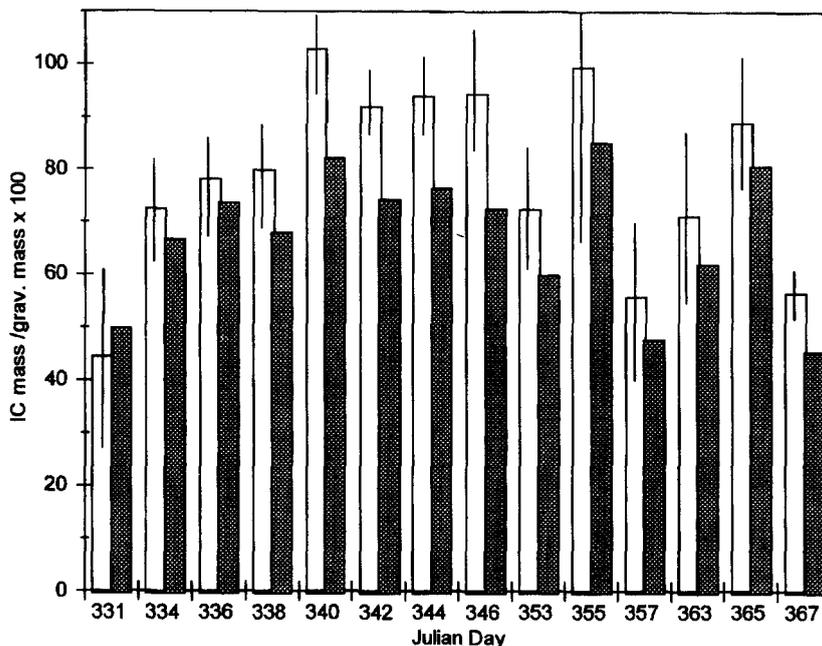


Fig. 9. Comparison of the ionic mass and the total mass for samples collected during the RITS experiment in 1994 at 19 and 48% relative humidity. The amount of water associated with the aerosol at 48% r.h. was determined from the difference in mass recorded at the two humidities.

aerosol may contain measurable quantities of water. When the relative humidity of the gravimetric determination was decreased from 35 to 9%, the aerosol mass decreased only slightly, as demonstrated in

Fig. 12. A linear best fit to the data indicated the change in aerosol mass, as the relative humidity increased, was 9% of the total (slope 1.09, y-int 0.002, $R^2 = 0.98$). This change is attributed to water

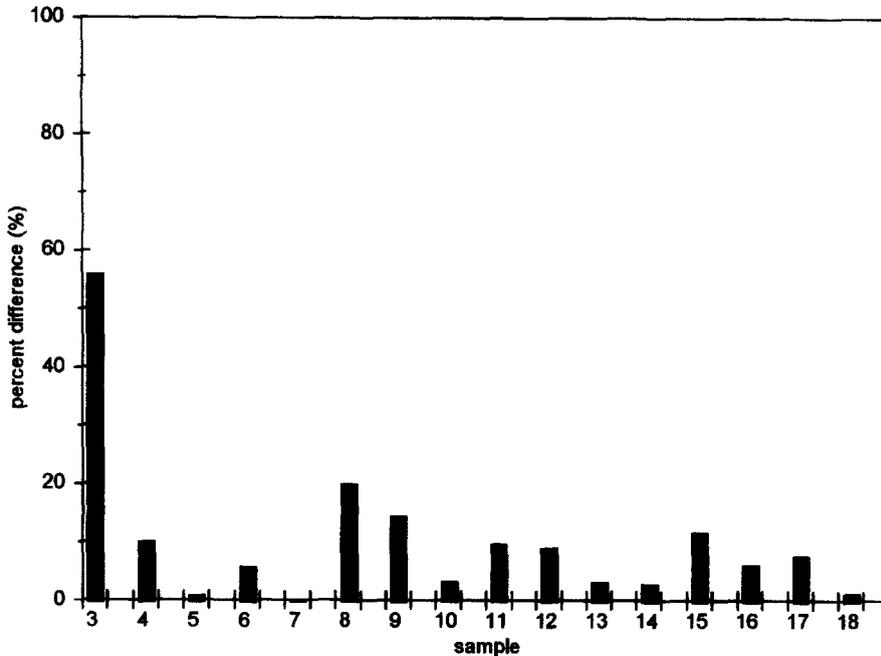


Fig. 10. Duplicate filters were analyzed by IC analysis demonstrating on average a 10% difference between the ionic masses measured on the filters.

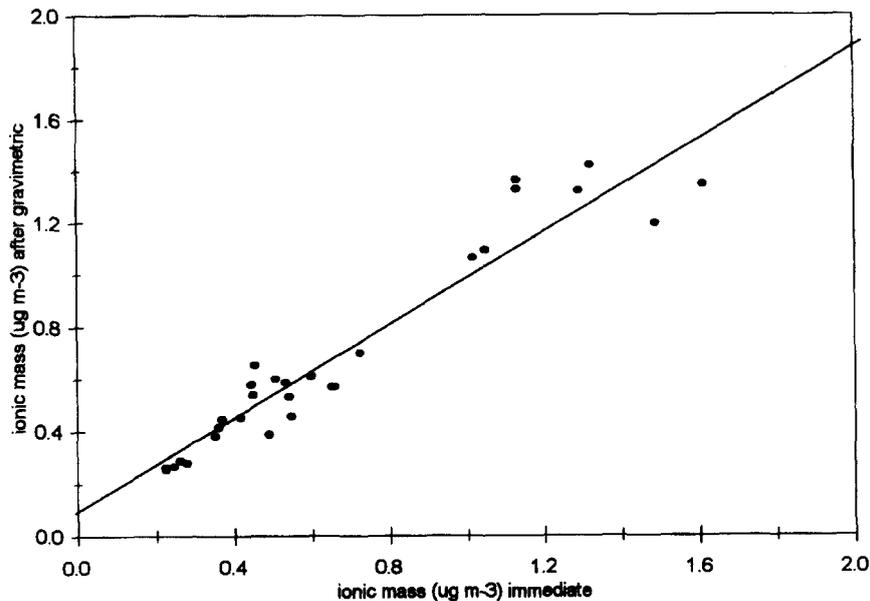


Fig. 11. Duplicate filters were collected with one for immediate IC analysis and its pair analyzed by gravimetric and IC analysis at a later time. The results were highly correlated ($R^2 = 0.96$) with a slope of 0.92 and y -intercept of 0.08.

associated with the aerosol at 35% relative humidity and should represent the amount of water associated with aerosol collection at approximately the same relative humidity.

Remote Pacific aerosol. The total submicrometer aerosol mass was measured for samples collected dur-

ing the RITS experiment in 1994 at $47 \pm 3\%$ and $20 \pm 2\%$ relative humidity. Assuming the particles were virtually dry at 20% relative humidity, the mass of water associated with the aerosol particles can be inferred from the mass difference between the two humidities. A linear best fit of the data (Fig. 13)

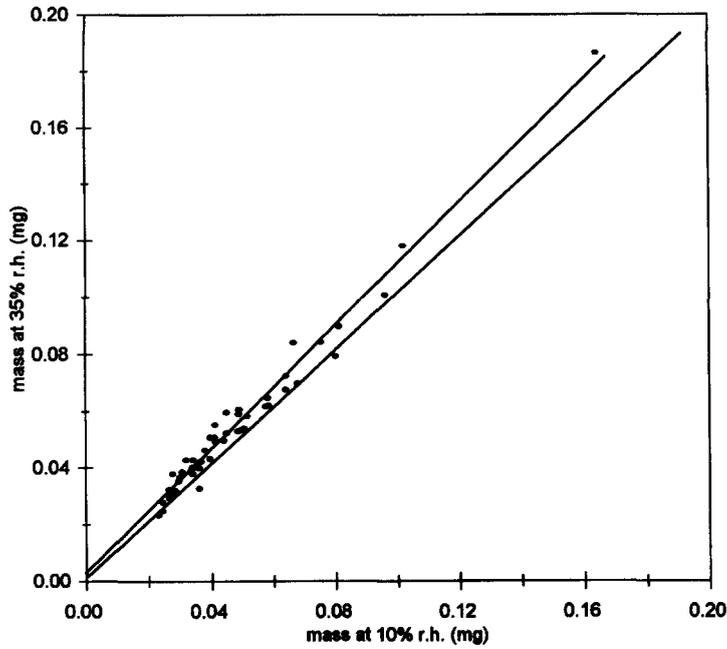


Fig. 12. A 9% change in aerosol mass was associated with increasing relative humidity from 9% to 35%. Samples were collected at Cheeka Peak in the winter and spring of 1994. A linear best fit of the data is shown along with a 1:1 line.

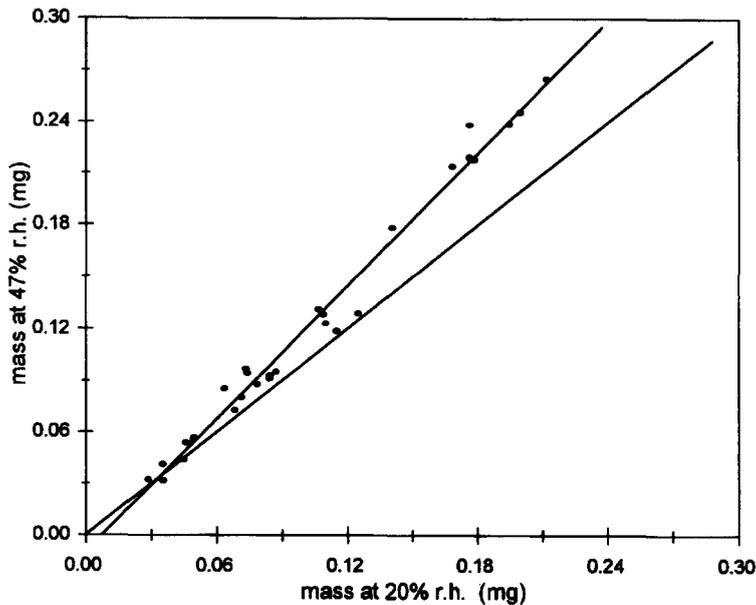


Fig. 13. Aerosol samples collected during the RITS experiment in 1994 had 29% of their mass as water at 47% r.h. assuming the samples were dry at 19% r.h.. A linear best fit of the data are shown along with a 1:1 line.

indicated the aerosol particles contained 29% water by mass at 47% r.h. (slope 1.291, y -intercept 0.010). The amount of water associated with the aerosol at this relative humidity would be somewhat larger if the particles still contained appreciable water at 20% relative humidity. The correlation between the two humidities is very good ($R^2 = 0.99$) suggesting the

hygroscopicity of the aerosol was consistent during the course of the experiment.

The total supermicrometer ($10.0 \mu\text{m} > D_p > 1.0 \mu\text{m}$) aerosol mass concentrations determined from samples collected at Cheeka Peak since January 1994 is reported in Table 7. The aerosol mass was between 2.3 to $6.2 \mu\text{g m}^{-3}$ demonstrating the supermicrometer

Table 7. Supermicrometer aerosol mass concentrations from samples collected at Cheeka Peak

| Start date | Stop date | Mass ($\mu\text{g m}^{-3}$) | Relative error (%) |
|------------|-----------|-------------------------------|--------------------|
| 94 02 03 | 94 02 09 | 2.28 (40% r.h.) | ± 3 |
| 94 02 11 | 94 02 22 | 5.00 (40% r.h.) | ± 2 |
| 94 03 16 | 94 03 22 | 6.17 (40% r.h.) | ± 2 |
| 94 04 12 | 94 04 19 | 6.08 (40% r.h.) | ± 2 |
| 94 04 23 | 94 04 29 | 4.41 (40% r.h.) | ± 5 |
| 94 05 06 | 94 05 12 | 6.11 (40% r.h.) | ± 2 |
| 94 05 20 | 94 05 26 | 4.01 (40% r.h.) | ± 2 |
| 94 05 27 | 94 06 01 | 6.23 (40% r.h.) | ± 2 |
| 94 06 02 | 94 06 08 | 2.54 (40% r.h.) | ± 4 |

aerosol contributes a larger portion of the aerosol mass as compared with submicrometer mass concentrations determined for the same period. Percentage wise the supermicrometer particles contribute about 61–86% of the total mass of the whole aerosol-size distribution.

CONCLUSIONS

Aerosol mass concentrations measured from the remote Pacific atmosphere and the marine/continental interface of the Washington coast were variable at 0.26–4.90 $\mu\text{g m}^{-3}$ for the submicrometer aerosol (2.28–6.23 $\mu\text{g m}^{-3}$ for the supermicrometer aerosol). A comparison was made between the ionic mass (and associated aerosol water) and the total aerosol mass, which revealed a significant portion of the aerosol from the marine/continental interface remained unaccounted for in the chemical analysis. Discrepancies were also observed for samples from the remote atmosphere over the Pacific during continentally influenced periods. The amount of water associated with the aerosols reflects particle behavior on a filter substrate and will not necessarily mirror the behavior of individual aerosol particles suspended in a gas. Better measurements of the amount of water associated with the ambient aerosol, as a function of relative humidity, are needed. Results from the land-based sampling platform (Cheeka Peak, WA) indicate a significant and variable portion of the total aerosol mass is due to aerosol components other than sea salt, sulfate, and water. Individual particle analysis confirmed the presence of mineral and carbonaceous particles (believed to be of organic composition). It is apparent that despite a carefully controlled sampling strategy, the samples were influenced by an airmass which at some point in its history passed over land. Long-range transport over the Pacific Ocean and transport from the North American continent are thought to be responsible for the increased abundance of mineral and carbonaceous aerosol found in the samples. Samples collected from the remote Pacific atmosphere demonstrate that these additional components often do not contribute significantly, but can represent up to 59% of the total mass depending on the relative sampling location and air mass history.

The amount of water contributing to the aerosol at the controlled sampling conditions was relatively consistent and low at Cheeka Peak (9% of the total mass at 40% r.h.) and somewhat higher for the remote Pacific atmosphere (29% of the total mass at 48% r.h.). On average the ammonium to sulfate ratio is higher at Cheeka Peak, which would cause the amount of water associated with the aerosol to be less. Future research efforts should address the role of organic material to the direct and indirect aerosol forcing, by evaluating its hygroscopic behavior and effect on aerosol optical properties.

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